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Review
Functional materials of porous metals made by P/M, electroplating and some other techniques

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Porous metals used as functional materials have been developed greatly and swiftly in recent years. In this paper, some preparative methods and relative applications are reviewed primarily for these materials. These methods concentratively deal with powder metallurgy (PM) and electroplating techniques, and these applications cover filtration and separation, fluid distribution and control, energy absorption, electromagnetic shielding, heat exchangers, electrode matrixes, reaction materials, biomaterials, and so on.

1. Introduction

In general, there are two types of porous materials: natural materials (e.g. sponge and aphrizite) and man-made materials. In terms of material assortment, they can also be divided into two types: metallic materials and nonmetallic materials (e.g. plastics and ceramics). Porous metals mean metallic materials which have beneficial pores or voids.

Porous metals consist of metal skeleton and pores/voids, and possess the basic metal characters like weldability and shape flexibility [1–4]. Compared with compact metals, the notable feature is the existence of a great deal of voids within the inner body for porous metals. This imparts the material many excellent properties, such as small specific weight, big specific surface area, high energy absorption, low heat conductivity (for close-cell bodies), high heat exchange and radiation ability (for open-cell bodies), excellent permeability (for open-cell bodies), good absorption of electromagnetic waves (for open-cell bodies), flame-stopping power, resistance to heat, heat shock or flame, gas sensitivity (Some of them are very sensitive to certain gases), possibility of regeneration, good workability and so on. Porous organic high-polymer materials are low in mechanical strength and not resistant to high temperatures. Porous ceramics are brittle and not good resistant to heat shock. So porous metallic materials have been widely used in many fields, such as aerospace technology, atomic energy, electrochemistry, petrochemistry, metallurgy, machinery, medicine, environmental protection, building trade and so forth. Their applications cover separation, filtration, gas distribution, catalysis, electrochemical process, noise erasure, impact-energy absorption, electromagnetic-wave shield, heat exchange and some other technical processes. They have been used to produce filters, catalyst supporters, porous electrodes, energy absorbers, silencers, shock-absorbing buffers, electromagnetic shielding or compatible elements, heat exchangers, flame arresters, etc [1–11]. Furthermore, they can be used to produce many composite materials or to serve as gaskets. They can be used as both functional and structural materials in many cases. In a general word, they are excellent and versatile engineering materials.

In this paper, two basic practical methods for preparing porous metals are introduced including powder metallurgy (P/M) and metal deposition techniques, and the functional applications are reviewed for these materials.

2. Producing methods [3, 5–10, 12]

Earliest, Davies *et al.* [3] gave a systematic classification to the methods for producing porous metals, and afterwards Ashby *et al.* [5, 6, 12] comprehensively summarized these methods in more detail. Among these, two main basic methods of P/M and metal-deposition techniques are emphatically introduced here.

2.1. Powder metallurgy (P/M)

Powder metallurgy is a manufacturing process making use of metal powder (or the mixture powder of metal with nonmetal) as the raw materials to produce porous metals, compound materials and various products by molding and sintering.

The porous metal made by P/M technique is early developed [3, 7, 9, 10]. Generally the pore size is smaller than 0.3 mm, and the porosity does not exceed 30%. Nevertheless, special manufacturing technology can be used to produce this kind of products with porosity far more than 30%.

In metallurgical and chemical industries, in order to reinforce some technological processes, high temperature and high pressure are needed, so the filtration and separation materials are also needed to be resistant to both high-temperature and high-pressure. In the process of catalytic reaction, the catalytic material with high specific area is needed to provide reaction with contact area as large as possible. In order to guarantee the safety and reliability of aeronautical facilities and fluid drive system, the variety of oil and working gas must be strictly fine-filtered. The high-temperature components of aircraft and rockets require an uniform porous material that is resistant to high-temperature and heat-vibration to serve as the matrix for heat dispersion and cooling; etc. Generally, the nonmetal porous materials like organism, ceramics and glass can not always suit the using requests of strength, plasticity and high-temperature simultaneously. The porous metallic materials produced by powder metallurgy may make up the shortcomings of the above materials to some extent, so have gained fast development.

2.1.1. Shaping powder-sintering [13–15]

Mixing the metallic powder and the foaming agent and shaping it, a shaped mixture body will be got. This mixture is heated in the reductive gas for metallic particles to diffuse and combine one another. After the decomposition of foam and the sintering of the metallic powder, a porous metal body is obtained. The metallic powder can be of molybdenum, molybdenum alloy, wolfram, wolfram alloy or their mixture. Also, the metallic powder can be of aluminium [16], and Fig. 1 shows the optical micrograph of an aluminium foam.

Besides, Kunze *et al.* [17] introduced a relatively newly developed technique of powder metallurgy [18, 19], which is suitable to produce high porosity porous metals. By this means, the commercially available aluminum powder or its alloy is mixed with foaming agent in a traditional way, and then pressed to form a semi-product with certain density. It is suitable to press it either in single direction or by a roller. After the semi-finished piece is heated to the temperature near the melting point and gets expanded, the high-porosity structure is formed.

Figure 1 Optical micrograph of an aluminum foam from PM process (ratio 4:1) [16].

2.1.2. Loose powder-sintering

Filling the metal powder in a mould and then sintering in non-pressure condition to make the powder particles stick to each other, a porous metallic material will be obtained. The porosity of the product by this method is from 40 to 60%.

In order to achieve high porosity, the commonly used means is to add puffing agent into the mixture. The puffing agent will decompose or volatilize during sintering, and can be also removed by sublimation or dissolution. For example, when the porous metal such as iron, nickel, copper or their alloys is produced, methycellulose is often used as the puffing agent, and the porosity can increase up to 70–90%.

2.1.3. Slurry-foaming technique

At first, a mixture slurry is prepared consisting of metal fine-powder, foaming agent and organism. The mixture is then heated and foamed to get a solid porous structure. This technique is used to produce several kinds of porous metals including beryllium, nickel, iron, copper, aluminum, stainless steel and bronze.

2.1.4. Sintering of slurry-saturated organic sponge

A sponge-like organic material is cut to the desired shape, and then soaked in a slurry containing the desired metal powder (the slurry vehicle can be water or an organic solvent). After the saturated sponge is dried and the solvent is removed, the organic sponge is heated to decompose or pyrolyse at some temperature. The residual metal body is sintered at an even higher temperature, and then cooled a high-porosity porous metal with interconnected cells will be obtained.

In the process described above, a metal compound can be used instead of metal powder. Metal lactic salt and carbonate are two examples. When the mixture is heated to the decomposition temperature, it can transform into the corresponding metal at the same time when the support structure is burned out. This method has been used to produce porous silver with porosity of 70–90%.

Another way to produce porous metals starts with preparing a suspension colloid of metal powder. This colloid is then poured into a cellular structure like foamed plastics with open-cells. After sintering the organic vehicle is removed, the particles of metallic powder are sintered to connect with each other [20]. During the process, the ability to maintain the completely open-cell structure is greatly limited. This is because that, with the increasing of the amount of metal powder or the decreasing of the pore size of the organic matrix, lots of the internal pores will get blocked by the metallic particles when the suspension colloid is continuously poured in. Thus the ability to reproduce the open-cell will get more and more difficult.

It is also feasible to fill the porous resin with metallic powder and then sinter, or uniformly mix metal powder with foaming agent and then sinter the mixture or heat it to its melting point. The porosity of the obtained metal foam can be up to 98% [21].

2.1.5. Fiber metallurgy [3, 7, 9, 22–25]

Generally speaking, the porous material made from metallic fiber has the better properties than that made from metallic powder. For instance, if the diameter of the metallic fiber is the same as the grain size of the metallic powder, the filtration material made from the metallic fiber will have the permeability over ten times more than that made from the metallic powder. In addition, fiber-sintering porous materials possess relatively high mechanical strength, corrosion resistance and stability at high temperatures. The porosity of this material can be more than 90%, and the internal pores are all interconnected. Further more, the material exhibits good ductility, good impact-tenacity and high dust-containing capacity, thus it can be used in many circumstances of strict filtration restrictions, and is titled as the "second generation of porous metallic filtration materials". The American Company MEMTEC is the earliest to develop this material. Later on, production lines were set up in Belgium, Japan and China for production on a large scale.

2.1.5.1. Preparation of porous body. Generally the process of this technique consists of three stages: fibers preparation, felt preparation and sintering. A fiber felt is produced by uniformly mixing and spreading metal fibers which have certain distribution of length and diameter, as well as a given range of length-diameter ratio. This felt is then sintered in a reductive gas to obtain the porous metal fiber material. This technique can be utilized to produce different porous metals like copper, nickel, Ni-Cr alloy and stainless steel. The porosity of the products can be controlled in a wide range. As an example, a stainless steel composite [26] from fiber precursors is shown in Fig. 2.

In addition, a new method for producing porous metal fiber different from the common metallurgical technique has been developed. It makes use of the pyrolysis of metal carbonyl to produce fiber porous bodies continuously. Nickel carbonyl gas and inert gas are sufficiently mixed up in a reaction chamber, then nickel carbonyl partly gets pyrolyzed and generates lots of crystal nuclei of nickel. The un-decomposed nickel carbonyl is further pyrolyzed and the produced nickel deposits on the crystal nuclei. These nuclei are gradually growing up to become long fibers that interweave to form a felt. This method can be used to produce the high-quality porous metal fiber material, but the size of the product is limited and the cost is high.

The above methods producing porous fiber materials are all easy to acquire the product with high porosity and continuous voids.

2.1.5.2. Preparation of metal fiber

- *Drawing*: A very thin metallic fiber, whose section-shape and surface-quality can reach the best status, can be obtained by common single wire drawing. However, the production efficiency is low and the cost on die is high, so the product is relatively expensive. To draw in batches, i.e. to draw tens or hundreds of wires simultaneously with one die, the production efficiency can be greatly increased, and the cost can be reduced.
- *Grinding*: To grind a metal body with a grinding machine equipped with some high-hardness abrasive material, by the adjustment of cut depth and transfer rate with the selection of grain size of the abrasive material, the metal fiber with desired diameter can be obtained. The thickness of the metal fiber is affected by many factors. For example, the larger the transfer rate, the thinner the fiber, and the thicker the grain of the abrasive material, the thicker the fiber. This technique can be used to produce thin fibers such as the fiber of nickel and nickel alloy, as well as the fiber of very tough nickel-iron alloy and so like.

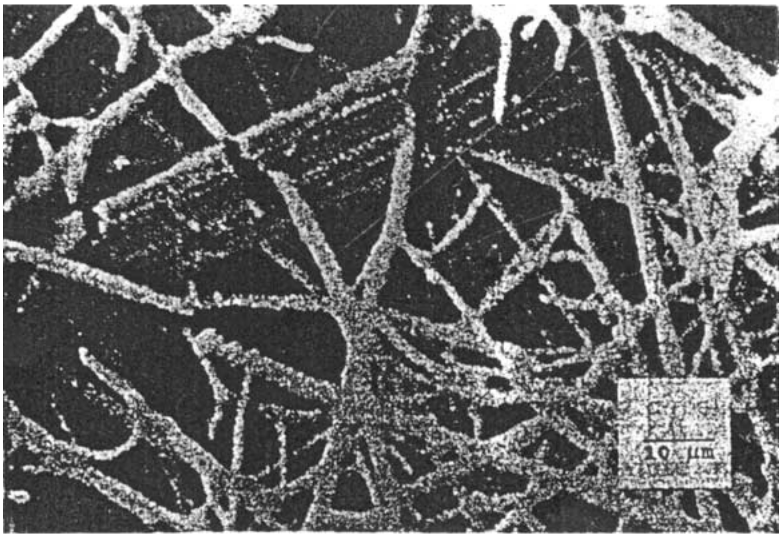

Figure 2 A stainless steel composite from fiber precursors [26].

- *Spinning*: Using mechanical force or gas pressure makes the melted metal leak out through the small holes of the bottom of the container, then cooling to make it solidify in a suitable atmosphere. The process of this method is simple and quick, and there is no pollution from waste oil or water, and no residual stress in the metal wire.
- *Machining*: A technique producing cheap metal fibers, called "high-frequency vibration cutting technique", was developed in Japanese Tokyo University in 1980s. This method makes use of elastic cutter with vibration frequency up to 2.7–3.0 KHz. There is a quantitative relationship between the diameter of fiber and the machining factors including cutting velocity, feeding rate and the vibration frequency of the cutter. This relationship can be expressed by a mathematical formula. When the cutting rate is 24 m/min and the feeding rate is below 10 μm per rotation, short fibers will be produced. The fiber is about 500 μm in diameter and the cross-section is nearly triangular.
- *Metal plating and sintering*: At first, organic fiber is processed by chemical plating, vacuum evaporation plating, metal-slurry saturating or electroplating after the conductive treatment on the surface. At the next stage, the processed organic fiber is sintered in reductive gas and the organism is removed by pyrolysis, or heated in air to burn or pyrolysis the organism and then is removed oxide by reductive annealing. All of the above processes can produce hallow metal fibers.
- *Chemical metallurgy* [27]: Metal powder or metal oxide is mixed up with organic bonding agent to get slurry. This slurry is extruded out through the micro-holes of a spinneret to produce semi-product fibers. Next the semi-product is heated at high temperature and the bonding agent is removed. After the residue is sintered in reductive gas, a metal fiber is obtained. It is still feasible to directly put the semi-product fibers into the reductive gas and heat to make the bonding agent decompose to prepare metal fibers.
- *Reaction-sintering*: This technique is used in the United States to produce nickel fiber. A paste consisting of the powder of $Ni(OH)_2$ and the bonding agent was prepared and extruded out to become fibers. After the fibers are sintered and reduced, the nickel fiber will be obtained.

Fig. 3 [9] shows the pore size distributions of several sintered porous metallic materials.

2.2. Metal deposition

After atomic metals deposit on the inner surface of porous organic matrix and then the organism is decomposed by sintering, the porous metal is obtained. The main feature of these porous metals is of three-dimensional network structure with porosity higher than 80%. This kind of porous metal is a new type of functional and structural one with excellent properties, and takes an especially important position in the field of porous metals. We can declare in a sense that it brings the synthetic property index of low density, high porosity, high specific surface area, good interconnection of cells and uniformity which people desired to the top status for porous metallic materials, and any other kind can not match or approach it. Nevertheless, its feature also results in the limitation of mechanical strength. This type of porous material was produced and utilized in batches early in 1970s. In 1980s, the growing application field and the requirement of utilization lead to its very rapid development. Nowadays, it is produced on a large scale in many countries. The typical products are foamed nickel (nickel foam) and foamed copper.

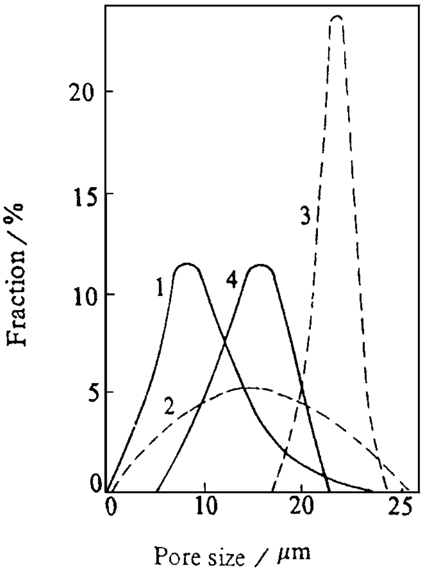

Figure 3 Pore size distribution curves for several sintered metal materials from fibres (curve 1), powders (curve 2), woven wires (curve 3) and sintered woven wires (curve 4) [9].

2.2.1. Sputter deposition

By the cathode sputtering, the metal atoms including inert gas is deposited on the matrix material under a partial pressure of the inert gas. Then the metal body is heated to a temperature above the melting point for a period of time sufficient for the entrapped gas to expand and form individual cells. After cooling, a metallic foam with cell-closed structure is obtained. The porosity of the metal foam can be controlled by varying the partial pressure of the inert gas in the deposition chamber, with the range from several percent to 80%.

With this method, the plasma of inert gas is produced to make the ionized inactive gas impact the target of evaporation-plated matter [28]. This leads to the sputtering of the particles of the evaporation-plated matter. The sputtering particles with high kinetic energy disperse the discharging gas and deposit on the matrix. The molecules of the inert gas hinder the particles to move straightforward and force them to flit in a round about way. So it is possible for them to deposit on the part of the "shadow". Since the rate of evaporation-plating is slow, the production efficiency of this technique is low.

2.2.2. Vacuum evaporation plating [28–30]

According to this technique, the matter used for plating is heated by electron beam or electric resistance to vaporize onto the matrix. Generally the plating layer from this process is very thin, especially when a synthetic resin is used for the matrix which will melts in the vacuum space. This is because the matrix is heated by the radiant heat resulting from the metal melting. The thickness of the cladding can only be up to 0.1–1.0 μm. A cooling media with the temperature of -30°C is induced into the cooling jacket of the vacuum chamber to reduce the temperature of the atmosphere in it, and the guide roller can directly cool. This makes the temperature of the organic matrix of net belt or porous material decrease below about 50°C. Therefore, no matter what kind of matrix or evaporation-plated metal is used, a thick cladding can be obtained with the cell deformation not easy. The porous matrix is removed in hydrogen gas then, and the resultant body is sintered and becomes the desired porous metal. The matrix can be a synthetic resin like polyester, polypropylene, polyurethane or an organism composed of cellulose. It can also be an inorganic matter made from glass, ceramics, carbon and minerals. The available metal for plating can be copper, nicked, zinc, tin, palladium, platinum, lead, cobalt, aluminum, molybdenum, titanium, iron, SUS304, SUS430, 30Cr, Bs and so on. After the vacuum vaporization plating, the product can be still plated a compound cladding which can be of Cu-Sn, Fe-Zn, Mo-Pb, Ti-Pd and so forth. To sinter the product in hydrogen gas, the matrix can be removed and both the strength and the ductility can be improved meanwhile. The temperature for sintering can be 300 to 1200°C. In terms of the application purpose, the last step may be omitted.

2.2.3. Reaction deposition [31]

A foam body with open cells is placed into a container filled with the gas of a metal compound, which is then heated to its decomposition temperature. The metal element is decomposed free from its compound to deposit on the foam matrix, and the metal-plated foam structure is formed. It is then sintered to form a metallic foam with open cells. To manufacture nickel foam, the metal compound can be nickel carbonyl, and the product consists of hollow nickel-wires.

2.2.4. Evaporation deposition [32]

The metallic material is evaporated slowly in an inert gas with high pressure of 102–103 Pa. During the movement of the metal atoms, they frequently collide with atoms of inert gas and ceaselessly change moving directions. This leads to the rapid reduction of the kinetic energy, and parts of the metal atoms will condense to form a "metal smoke". Affected by gravity and transferred by the current of the inert gas, the particles of the smoke move downward with the continuous decline of temperature, and reach the base bottom at last. Because of the low temperature at the bottom, the atoms are difficult to move or spread any longer, thus the particles of the smoke have to pile up loosely to form a foam structure with high porosity.

2.2.5. Electrodeposition

At present, this technique is commonly used on a large scale in many countries to produce porous metal with high porosity. The product possesses not only high porosity (from 80 to 99%) but also uniform reticulated structure, with cells all interconnected one another. The high porosity matrix with open cells is adopted, generally it is an organic foam with three-dimensional reticulated structure. The commonly used matrix can be polyurethane (including polyether polyurethane and polyester polyurethane), polyester, olefin polymer (e.g. polyethylene or polypropylene), ethenyl polymer, phenylethene polymer and eurelon. Fiber felt is also available. The process consists of four main stages, i.e. pretreatment of matrix, treatment for electrical conductivity, electroplating and reductive sintering.

At first acid or alkaline solution is used to process the matrix in order to remove oil stain, roughen the surface, etch and open the closed cells, and then the matrix is further cleaned with water. If the matrix is electrical conductible, the treatment for conductivity is not needed. As for the organic foam that is commonly used, this treatment is always necessary. It can be carried out by various methods, such as evaporation plating (e.g. vacuum evaporation plating), ion plating (e.g. arc ion plating), sputtering (e.g. magnetic sputtering), chemical plating (the metal used can be copper, nickel, cobalt, palladium, etc), coating conductible colloid (e.g. carbon-black colloid or graphite colloid), coating conductible resin (e.g. poly-pyrrole, poly-thiophene) and coating metal powder (e.g. powder of copper or silver), etc [1, 33–38]. The most commonly used methods are chemical plating and coating conductible colloid. Flat fine carbon particles are used in the conductible colloid to make the most particles have the surface contact when the colloid coats the skeleton surface of the synthetic resin [39]. This results in a smooth conductible layer, on which an even smooth and uniform cladding can be formed by the sequential electroplating, and a porous metal with three-dimensional network structure can be obtained eventually. It has high tensile strength and bending resistance. If the chemical plating is adopted, several steps must be taken in advance, including removement of oil stain, roughenation, sensitization, activation and reduction (dispergation) [40], which are described in detail in many literatures dealing with the technology of plastic electroplating.

Furthermore, a conductible high-polymer layer can also be produced by chemical oxidation polymerization on the surface of voids within the porous matrix. The same conductive layer can be formed by way of electrolysis polymerization and subsequent electroplating [41]. As the monomer of the oxidation polymerization, it can be pyrrole, thiophene, furan and other kinds of mixed pentacyclic compounds or their derivatives. The polymerization of conductible high-polymer materials is also introduced in [42] and [43].

The treatment for conductivity can make use of monomers as described above, and can also use polymers instead [44]. According to the previous method, the high polymer is saturated in the solution or the steam of the monomer of synthetic conductible polymer, which is polymerized to become the conductible polymer by catalysis. In terms of the latter method, instead of using the solution of the monomer of conductible polymer, a suspension solution prepared from the conductible polymer is used. There are no special restrictions on the conductible polymer except that it can be removed by heating. It can be poly-phenylamine, polypyrrole, poly-thiophene and poly-furan or derivatives of their alkyl, alkoxyl or phenyl and so on.

The electroplating can be carried out by means of commonly used mature technology. To electroplate a foamed body, with the increase of the electrical current density, the current density on the surface of the foamed body will get excessively high, and an undue polarization leads to the shortage of metallic ions. So, to electroplate a foamed body that is not conductible itself but has been treated on the void surface for conductivity, the available current density must be between 1/10 and 1/100 that for panel or wire stocks [28, 45]. To decrease the phenomena of concentration polarization, impulse current [46] and/or sprayed electroplating solution [47] can be used.

To change the ingredient of the electroplating solution, electrodeposition can be used to produce many high-porosity porous metallic materials including metals like nickel, chrome, zinc, copper, tin, lead, iron, gold, silver, platinum, palladium, rhodium, aluminum, cadmium, cobalt, indium, mercury, vanadium, thallium and gallium, and alloys such as brass, Co-Ni alloy, Cu-Zn alloy and others. Special electroplating solution can be used for the metals that can not be electrolyzed in water solution, for example, aluminum or germanium is generally electrolyzed in organic electroplating solution or in melted salt.

In the stage of reductive and sintering, the porous composite body that has been electroplated well can be directly placed in the reductive atmosphere to pyrolyze the organic matrix, and sintered to produce the porous metal. As an alteration, the electroplated porous body can be also first burned in air for the organic matrix to be removed, and then the resultant body coated with an oxide layer is sintered in the reductive gas [48]. If the thickness of the matrix is below 3 mm, the warping will be serious during roasting. As an improvement, several sheets of matrix may be overlapped each other for roasting, and the warping will be reduced [49].

Different reduction treatments have been studied in Japan [50]. The results showed that it was difficult for a uniform chemical reaction on the oxide layer to be evoked because the reduction ability of the gas-phase reaction between the reductive gas and the oxide layer is too weak. If a liquid–phase chemical material with even stronger reduction ability is used to process the oxides on the surface of the metallic skeleton, the oxide layer may be thinned more smoothly in comparison with the gas-phase reaction. Based on this idea, two plans can be conceived. By the first plan, the foamed resin skeleton is first electroplated and then roasted in air for the resin to be removed by pyrolysis. The obtained metallic skeleton is sequentially processed by a mineral acid (e.g. hydrochloric acid, sulfuric acid, nitric acid or their mixture). By the second plan, the porous metal covered with an oxide layer is first processed by heat treatment in reductive gas, and then soaked in a mineral acid solution for further processing.

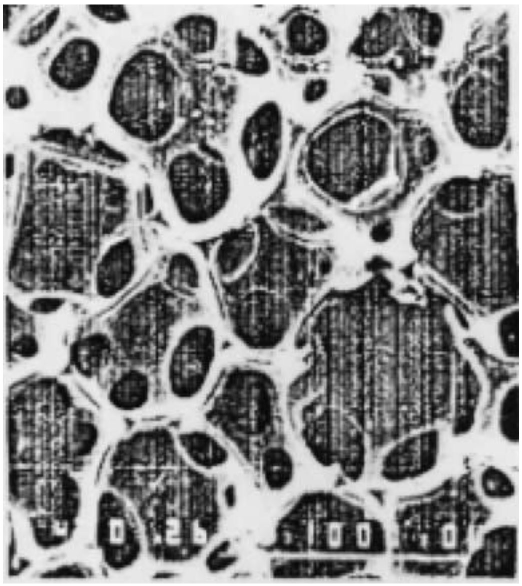

Figure 4 SEI of a foamed Cu-Ni alloy from electrodeposition process [51].

Figs 4 and 5 show the typical morphology of porous metals by electrodeposition [51, 52].

In order to improve the global uniformity of the cellular structure for the porous product, several sheets of foam electroplated can be piled up to get a desired thickness for second time electroplating to produce the porous metal [53]. In addition, the matrix can be stuck with each other to form a laminated entity, which is then plated by means of vacuum electroplating or by means of jet flowing electroplating after preconditioned for conductivity. In this way a porous metal with uniform cellular structure can be obtained [54–56]. There are several methods that are available to stick: to melt the surface with flame to join them; to bind them with solvent-series or emulsion-series binder; to merge them with hot-melt agent. Comparatively, to join them with flame is the best one since the membrane formed by emulsion binder will harm the porous property of the matrix.

2.3. Synopsis of other methods

Besides the above common techniques, there are many other methods which can be used to produce porous metals. Here are some examples: specific casting technique [3, 57–62], liquid-state processes [63–66], gas expansion methods [4, 19, 63, 64], self-propagating high temperature synthesis (SHS, also named combustion synthesis) [67–73], solid-gas eutectic solidification process (GASAR) [74–76], and some other methods [77–83]. The detailed information can be seen in the above corresponding quoted literatures.

3. Applications

Based on Refs. [1–11], the following paragraphs systematically describe the different functional applications for porous metals.

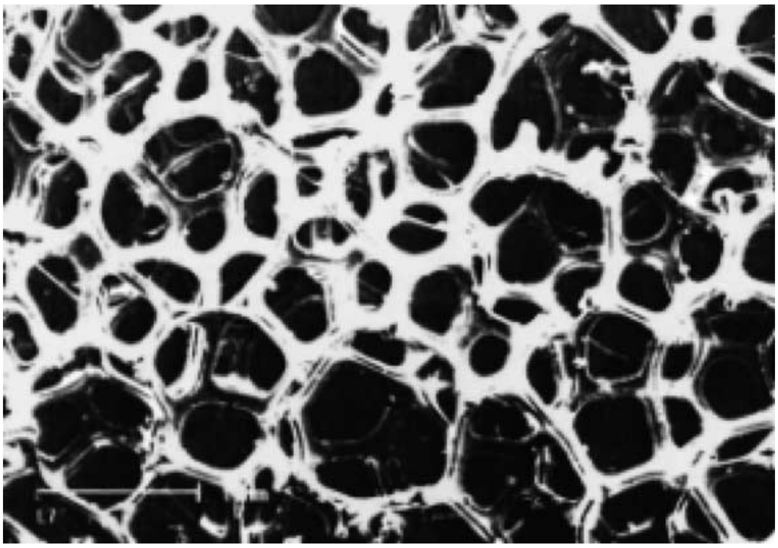

Figure 5 Overall SEM morphology of a nickel foam from electrodeposition process [52].

3.1. Filtration and separation

Porous metals possess very excellent permeability, and are the ideal materials to produce various filters. Their internal pore canals can stop and arrest solid particles in flowing media so that the gas or liquid can be filtered and separated. Porous metallic filter can be used to filtrate liquids (e.g. mineral oil, gasoline, refrigerant, melted polymer, suspension liquid and so like) or air or other kinds of gases to remove the solid particles. The most widely used metallic filter materials are porous bronze and porous stainless steel. Some porous metallic materials can serve as separation media, e.g. for separating oil from water or water from refrigerants. Some of them can also be used as diffusion media for aerating liquids or for distributing CO_2 in liquids. In the biochemical field, metal foam is used as a support for the osmotic membranes in kidney machines. This principle can also be extended to those processes relying on osmosis or reverse-osmosis, such as desalination and dehydrogenation during effluent treatment.

Liu *et al.* [84] studied the technology for producing a porous W-Ni-Fe alloy. They started with fine powder of W, into which 1–2% Ni-Fe (wt) was added. After pressing, pre-sintering, grinding, classifying and intensified sintering, they got the prefab alloy powder. This alloy powder was then added with 2% (wt) stearic acid or 0.4% (wt) poval. Through shaping, pre-sintering and sintering, the porous W-Ni-Fe alloy was obtained. This product can be used to purify the combustion gas of which the temperature is as high as 1523 K and the pressure is as high as 11.8 Mpa. Li *et al.* [85] chose the water-atomized powder of 0Cr18Ni9 stainless steel as the raw material. Shaped by steel-mould pressing or isostatic pressing, then sequentially sintered in vacuum or in pure hydrogen gas, a porous stainless filtration material was produced. This material possesses high strength, good thermal conductivity and excellent resistance to corrosion, and has been applied to the production of polyester film in petrochemical industry. Now, this material has been produced in China, and achieved a considerable economic benefit.

As filter materials, porous metals have many applications. Those matters that can be filtered include steam or liquid nitrogen at high or very low temperatures, organic solvent with strong dissolving power, melted polymer with high viscosity and great loss of pressure, fluid with notably variable pressure or flux, highly polluted fluid, the grains of catalyst to be recovered, and so on [86].

A cheap and practical diesel particular filter (DPF) system was developed in Japanese Sumitomo Electrical Industry Corporation for the first time in the word. It is easy to purify the exhaust gas of diesel engines. The material used is porous Ni-Cr-Al alloy with three-dimensional network structure whose porosity is 85%. The purified exhaust gas is up to the standard issued in 1997 [87]. The method to install a DPF system on the exhaust pipe was studied more than ten years ago, and the adopted filter material was ceramics. If too much soot was arrested, local temperature-rise would happen at the combustion part, and excessive temperature-difference would occur because of the low heat-conductivity of ceramics. This make the filter cracked and melted.

Ban *et al.* [88] invented the porous bodies of Ni-20Cr and Ni-33Cr-1.8Al alloys, which are able to resist the high-temperature corrosion of diesel exhaust-gas without the cracking problem of ceramics, and can be used as the filter material to greatly deduce environmental pollution.

The air purified by the filter made of the porous metal like bronze, stainless steel or nickel has been extensively used for the growth of anaerobic bacteria. This filter has replaced that produced by active carbon and degreased cotton. Making use of porous stainless steel or porous titanium as the decarbonizing material in the major liquid transfusion, the filtration effect is improved several-fold, and the cost of maintenance is reduced. This kind of filter has replaced the original sand leach rod. In metallurgy industry, when tantalum powder is smelted by wet process, the porous nickel filter is used to filtrate melted sodium. Porous titanium is used for the filtration of zinc sulfate solution during zinc smelting. In steel works, porous stainless steel is used for the purification of coal gas of blast furnace.

In atomic energy industry, filters made of porous nickel, Monel metal and porous stainless steel are used for the abstraction of UF6 and the filtration of the tail gas released by the vulcanization bed, which is used for the denitration of oxygen-uranium base nitrate. Filters made of porous metals such as low carbon steel, chromized iron, stainless steel and molybdenum, are used for the filtration of the dioxide cooling-gas in atomic power station and for the removal of the small pollutants with radioactive rays existing in the purification liquid of a reactor.

In aerospace industry, porous stainless steel is applied to the purification of the hydraulic oil in aircraft or guided gyroscopes, the purification of gas in the automatic fuel pipelines and the recovery of catalyst used in hydrocarbon combination process.

After 1980s, with the development of industries for petrochemistry, textile and papermaking, the need for heat-resistant, pressure-resistant and corrosion-resistant porous materials ceaselessly grows while the quality requirement is also raised. These promote a large scale of production for porous metallic materials. In the textile industry, pipes of porous stainless steel produced by powder sintering are used for the pre-filtration and scatter of spinning jets and for the removal of colorant particles in hot washing water. In papermaking industry, porous metals of 316L, 317LN alloys and titanium are used for paper-pulp rinse and sewage treatment.

In petrochemical industry, porous materials of low carbon steel or stainless steel are used for the removal of silt and sediment in oil drilling well. Porous iron filter is used for the separation between oil and wax in oil extraction and purification. Natural gas is filtered by the porous chromized low-carbon steel and several layers of metallic network. Porous materials made from powder or fiber of stainless steel are used for the filtration of liquid and the melted high polymer like polyester in the production of polypopylene. Porous stainless steel is also used for the collection of catalyst dust and the filtration of gaseous or liquid ammonia during the production of phthalandione anhydride and hexanolactam. The filter material used for the preparation of liquid sulfur or butyric acid is porous titanium.

In chemical industry, many kinds of chemical matters including nitric acid, 96% sulfuric acid, ethylic acid, boric acid, nitrous acid, oxalic acid, alkali, hydrothion, ethyne, vapor, sea water, molten salt, sodium hydroxide, gaseous hydrogen fluoride and so on, are all filtered by the corrosion-resistant porous metals like stainless steel or titanium for the purpose of purification or recovery.

By the adjustment of pore size and the usage of surface tension, the effect of separation can be obtained for medium. This principle can be used for the gaseous diffusion separation of U^{235} and its isotope U^{238} using the porous nickel with the pore size of 0.01–0.02 μm.

Generally speaking, in any situations of solid-liquid, liquid-liquid and gas-liquid separation and filtration, porous metallic materials can be utilized.

Porous titanium is a new type of filtration and purification material to replace the old generations. It can serve the chemical reaction with high degree of dispersion [89]. The strong resistance to corrosion is its outstanding characteristic. It can be used to filtrate various media, such as sea water, chloride, hypochlorite, wet chlorine, oxidative acids, oxidative alkalis, various organic acids, strong oxidative agent and various high-temperature or low-temperature media. It possesses excellent physical and mechanical properties, which can meet the relative requirements of filtration engineering. With the high filtration precision, it is suitable for both fine-filtration to remove bacteria and common rough-filtration like the sediment filtration. Making use of fine-filtering porous titanium to filtrate air, the bacteria like bacillus and bacteriophage can be reliably removed. The high strength and stiffness make it possible to self-support and can endure pressures from any directions. It is apt to various recovery methods like acid pickling, alkali washing and other chemical cleanings. It can also be cleaned by ultrasonic, recoil of high-pressure water or gas and solvent. An available method can always be easily found for the recovery in any cases, so the lifetime is very long for this material. As a filter material, porous titanium has a very wide range of applications. It can be used not only in the fields of chemistry, metallurgy, halite production, environmental protection, pharmacy, food fermentation and meticulous chemical industry for the purpose of fine or rough filtration and purification, but also in the fields of alkali-chloride industry, chlorination technology and the fine-filtration of aviation gasoline to replace the traditionally used gas-diffusion elements made of stainless steel for more benefits.

3.2. Distribution and control of fluid

Porous metals are also widely used in fluid distribution apparatuses. For instance, porous stainless steel is used to control the cooling gas or liquid for the shell of the nose-cone yaw-meter of rockets. Porous powder-metallurgy materials are massively used for the air-float roller of the plastic float membrane in tape processing equipment. Other distribution elements are used to aerate liquids. For example, the porous nickel pipe is used to aerate beer, and the porous plate of stainless steel or titanium is used to uniformly oxygenate blood by medical oxygenators, and so forth.

In petrochemical and metallurgy industries, the technology of fluidized bed is widely used. The commonly used plates for fluid distribution are porous metallic types made by the sintering of powders of various metals including bronze, nickel, Monel alloy, stainless steel and so on.

Porous metals are also used for fluid control. For example, they are used to produce meters of gas or liquid and delay timers for signal control in an automatic system.

3.3. Energy absorption

Energy absorption is an important application of porous metallic materials. For example, bumpers and bump levellers are the typical energy-absorbing apparatuses. Their applications cover bumpers of automobiles, landing gears of spaceships, safety pads of lifters or conveyers and the energy-absorbing lining of the protective hood for high-speed grinding machines. Metallic foams used in automobile components to absorb the energy of an impact or in protective devices to attenuate the shock wave from a blast may have complex shapes [90].

If an element located at the impact zone of car bodies is made of foamed aluminum, its deformation resulting from the highest energy-consumption will be controlled. The situation is the same for the protection against the side impact [17]. For example, to fill hollow steel or aluminum shells with foamed aluminum can enable these parts to behave well in deformation when they are loaded. Car bodies and other parts of engines can be manufactured or reinforced from foamed metals to obtain a high stiffness and a light weight. Modulus of elasticity can be selected in a large range by means of choosing the density of foamed metal to match the resonant frequency of foam elements. In this way, harmful vibration can be restrained.

The growing demands for vehicle safety and automobile industry lead to an increase of vehicle weight, so materials of low specific weight and high energy absorbing capacity are of special interest. Foamed organic materials have low specific weight, but the energy amounts convertible to deformation energy are also relatively low. Applying aluminum foams, which is made by P/M techniqure with porosity of 90% [18], energy absorbing devices with a corresponding higher energy level can be realized [91]. Maiti *et al.* [92] have proposed energy absorption diagrams for the determination of optimised energy absorbers, and a comprehensive treatment of energy absorption by foams is given in Gibson and Ashby [5].

Applying foamed metals to the shock-resistant light part as the impact-energy absorbing structure, the shock resistance is increased, and the safety insurance against collision is improved, for automobiles [93, 94].

Silencing of noise is another important application for porous metals in respect with energy absorption. Foamed metals possess excellent acoustic properties that can match those of polymer foams, which are the best sound-control materials, and can preserve these properties at high temperatures. As a sound-absorbing material, it must have a series of good properties for sound absorption efficiency, entrant sound loss, gas permeability, fire resistance and structure strength simultaneously [95]. Nonmetal fiber materials like glass wool are of bad deformability, and their sound absorption efficiency will be spoiled under the condition of rainwater. The sintered materials like ceramics are of low impact strength. Therefore, porous metals are broadly used in buildings, automatic office equipments and radio recording rooms. They act as not only outside decorations but also sound-absorbing materials.

Sound absorption means an incident sound wave is neither reflected nor transmitted, its energy is absorbed in the material. Foams having low initial relative densities are found to be better sound absorbers than those with high relative densities [96]. On the other hand, at the same initial relative density, sound absorption is maximized by a foam with an optimal thickness. This is shown in Fig. 6 for a commercially available aluminum-foam of trade name Alporas foam [96].

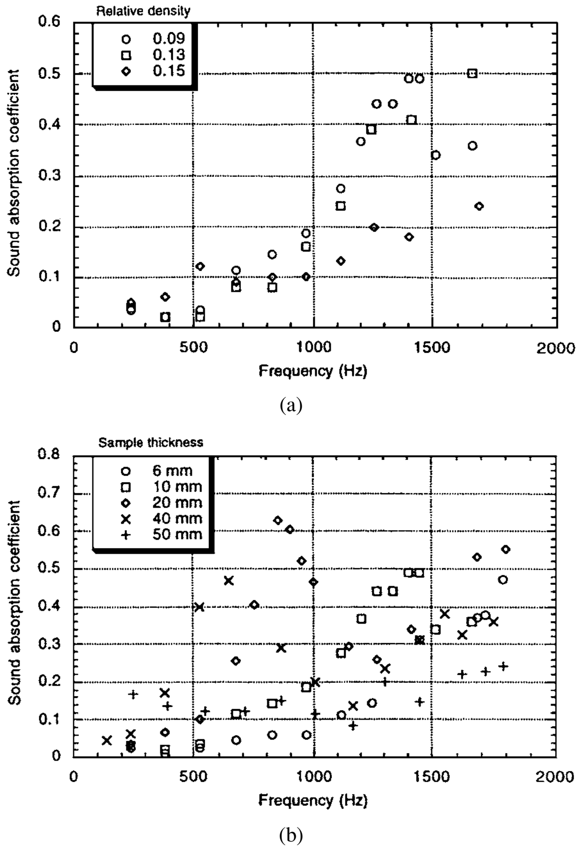

Figure 6 Sound absorption coefficient of a commercially available aluminum foam (Alpora foam) plotted as a function of frequency for selected values of (a) relative foam density at fixed foam thickness 10 mm and (b) foam thickness at fixed relative density 0.09 [96].

For the sound-eliminating materials used under special conditions like the exhaust system of gas turbines, they must meet the composite demand of high efficiency, long lifetime and light weight. Common sound-absorbing components or materials are not suitable. Since the light porous titanium is resistant to corrosion and scour of high-speed airflow at high temperatures, it is satisfied to be used for the noise control of exhaust systems of turbine [97].

For more than ten years past, the technology of speed increase and weight reduction for trains has been studying in Japan. However, this brings rail-vehicles the more serious vibration and noise. Thus, the demand to control the noise caused by automobiles and trains became an important subject for this technology. A foamed aluminum alloy developed by Naoe [98] possesses a very good sound-elimination and vibration-absorption efficiency. It has been used as the damping materials for automobiles and trains to solve the above problem.

In the ultrasonic inspection and measurement, foamed metals have been used as the receptor materials [17] because their ultrasonic resistance locates in the suitable range.

Furthermore, the gas transported over long distances through high-pressure pipeline can produce high-intensity noise, which will travel along the pipeline.

Using foamed metals to transport gas by gas-diffusion way, the noise can be almost completely eliminated. Foamed metals can also be used in other cases of pressure reduction, e.g. serving as the muffler for steam power stations and air tools. For example, mufflers for air tools can be made from foamed copper with the density of 5%. If they are used as muffler materials, sufficient airflow must be guaranteed based on the acquirement of silence effect.

Maiti *et al.* [92] had the research result showing that, how the energy absorbed, per unit volume of foam, depends on the density of the foam and on the stress, and there is an optimum foam density for a given packing or energy-absorbing application.

3.4. Electromagnetic shielding

Porous metals can be used in electromagnetic shielding or compatible components.

With the high-speed development of modern electronic industry, electronic appliances are widely used, and the problem of electromagnetic radiation gets more and more serious. It not only interferes with other electronic equipment, but also results in information leakage, so the methods of electromagnetic shielding are very significant. Porous metals available in this field are mainly the three-dimensional reticulated copper or nickel with the internal cells all interconnected one another. This structure is of good permeability, high dissipating capability and small specific weight. Its shielding power is much bigger than that of metallic networks, and can match that of wave-guide windows. Compared with wave-guide windows, porous copper or nickel mentioned above has the smaller volume and is more portable, so it is more suitable to be used in moving instruments or equipments [99].

3.5. Heat exchanger

The thermal conductivity of porous metals is quite large compared with their polymer and ceramic counterparts [5], and their thermal diffusivity is comparable to that for dense metals [6, 100]. Additionally, these materials possess a large specific surface area. Hence, porous metals are the efficient materials for heat exchange and radiation. Cell-opened porous metals are suitable for heat exchangers, heaters and radiators. Among them, both circulatory air heater and electric-resistance water heater display very high efficiency and excellent employability. They can be combined with tubulous or flat metallic products to form assemblies, which are advantageous for 3-D complicated flow to overcome the harmful influence of boundary layer on the condition of forced convection. Cell-closed porous metals can be used as heat-insulating materials, whose strength and heat resistance are better than those of traditionally used materials.

Foamed steel is adaptable to a very wide range of temperature, and can be used to manufacture exhaust manifolds of automobile engines. Since the heat conductivity of the manifold is reduced a great deal, the time required for the temperature to rise to the level of normal operation of exhaust catalysis is relevantly shortened.

Besides, porous metals are fireproof and possess high permeability consistent with flame-stopping ability. So they can be utilized to prevent flame propagation along pipelines, and can be also used to manufacture fire extinguishers.

The overall thermal conductivity in porous media is one of the major concerns in heat conduction because poorer conductivity may cause unexpected accumulation of thermal energy in the areas where concentration of pores is dense [101]. The cavities of porous metals are assumed to distribute randomly and uniformly so that the overall thermal conductivity remains isotropic.

Lu *et al.* [11] developed an analytical model for model foams with simple cubic unit cells consisting of heated slender cylinders, based on existing heat transfer data on convective crossflow through cylinder banks. For typical uses of metal foams, heat transfer due to radiation at the cylindrical surface is usually at least one order of magnitude smaller than that due to forced convection, and the heat transfer coefficient depends weakly on temperature. The experimental result displays that the pressure drop per unit length as function of relative foam density had a minimum value for fluid flowing across the porous metal (see Fig. 7).

High levels of basic understanding about thermal property, as well as mechanical and acoustic properties, has been developed [6, 66, 100, 102–104] for cellular metals.

3.6. Electrode matrixes

Another application of porous metals is for porous electrode materials. Various storage batteries, fuel cells and air cells, all use porous nickel as the electrode, with the porosity as high as possible.

In the fields of high technologies and civil applications, continual requirements are put forward on high energy-density, long lifetime and low production-cost for the secondary alkaline batteries, such as nickel-hydrogen and nickel-cadmium types, and the traditionally sintered nickel plates are challenged. To adopt the plates made of foamed metals or metallic fibers instead of the traditional sintering materials, the consumption of nickel decreases half while the weight of plate reduces about 12%, yet the energy density greatly rises [105]. Here are two examples: In Germany Hoppecker storage battery plant, the porous nickel plate with porosity of 90% was used as the electrode matrix of NFC-type nickel-cadmium battery. Compared with the sintering plate, the weight specific capacity increased by 30% for nickel electrode. In Japanese Yuasa Company, the porous metallic plate was used for the cadmium electrode. Compared with the sintering plate, the specific energy increased by 33% [106].

The foamed copper produced by electrodeposition on organic foam can be used as the cathode for electrolyzed copper reduction and the electrode for organic electrosynthesis. Foamed nickel is used as the flow-through and flow-by porous electrodes in chemical reaction engineering. This kind of electrode possesses excellent properties for electrolyte diffusion, migration and matter exchange [107–110]. Langlois *et al.* [111, 112] further studied the potential distribution

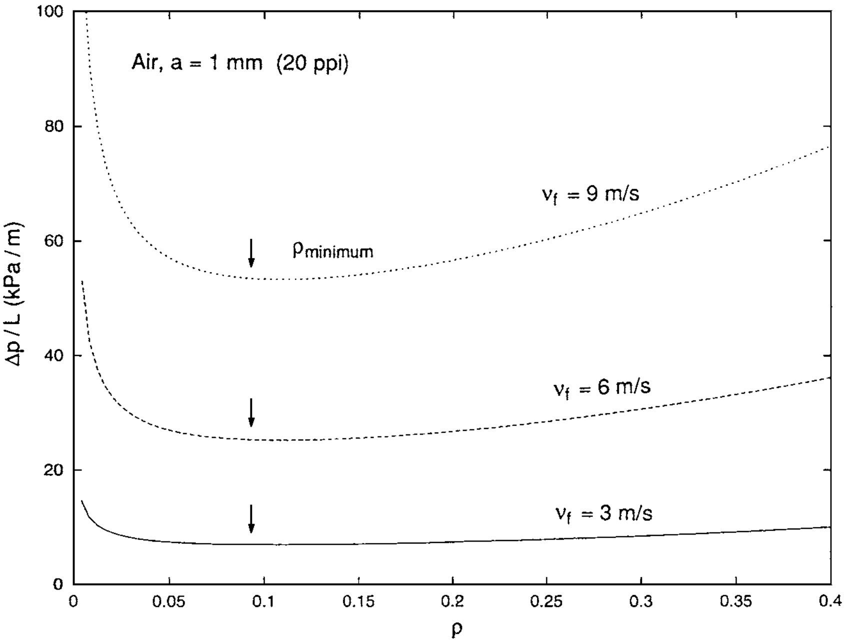

Figure 7 Selected results on pressure drop per unit $\Delta p/L$, as functions of relative foam density ρ and fluid velocity v_f for air (20°C) flowing across a duct filled with 20 ppi ($a = 1$ mm) ERG aluminum foam [11].

of the flow-through electrode made of foamed nickel. The result showed that the potential distribution in the porous electrode depended on the Ohmic resistance of the porous material to a great extent on condition that the thickness of the electrode was small.

To apply foamed nickel to electrochemical reactors, the function of electrochemical unit is improved due to the increase of the surface area of electrode. Foamed nickel can also be used without membranes in some industrial applications [113]. Still more, foamed nickel is apt to serve as the three-dimensional porous anodes for the electro-oxidation of organic compounds. For example, the multiphase electro-catalytic oxidation of benzyl alcohol promotes the generation of acetaldehyde, and the foamed-nickel electrode makes the current strength of electrolysis and the conversion rate of alcohol increase nearly 30% [114].

Also, foamed nickel is applied to the electrode of high-pressure Ni-H_2 battery [115] and the diffusion electrode of fuel cells [116], which serve spaceships. As the support of the active substance in lead-acid batteries, porous lead can greatly lighten the electrode [117].

The electrical resistivity of the electrode matrix is a basic property, sometimes of key importance. Study on the relationship between this property and porosity for porous metals with high porosity [118–120], it is found that the resistivity increase faster and faster when the porosity increase (see Fig. 8).

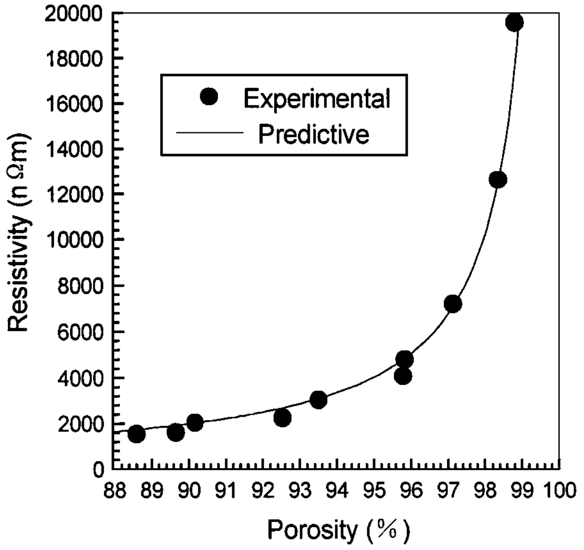

Figure 8 Plot of electrical resistivity as function of porosity on nickel foams [118].

3.7. Reaction matrixes

In chemical industry, porous metals can be used to manufacture efficient catalyst or catalyst supporter because of the high specific surface area and the self-support strength. Sometimes, porous metals themselves, such as porous Raney copper [121] and porous nickel [122], are catalysts. The porous Cr-Ni stainless steel [123] is an example of catalyst supporter. The catalyst based on porous metals can be used in many reaction engineerings, such as the deep oxidation of hydrocarbon, selective oxidation of alcohol [124], hexane recombination [125] in petrochemical process and so on. Making use of foamed metals to manufacture catalytic averagers of the toxic exhaust of automobiles, the discharged CO decreases 2 to 3 times, and the toxicity lowers 90% [126]. In the field of environmental protection, foamed nickel is used in the oxidation-reduction of the six-valence Cr ion (highly toxic) in water solution [127], and porous titanium with uniform structure is used in the apparatus of industrial waste-water treatment [128].

It was reported in the Japanese Journal of Engineering Materials (Vol. 38, No. 12) that, New Japanese Corporation of Iron and Steel cooperating with Panisonic Electrical Corporation developed a new deodorant material with good performance and long lifetime. It is composite using porous iron-base body with three-dimensional network structure as matrix, which is combined with fine powder of iron and complex compound of organic acid. This material can be applied to many cases like in multi-functional deodorization, automatic air-purifiers and deodorant building-materials [129]. The process to produce this deodorant material starts with the slurry of fine iron-powder of size below 10 μm. In this slurry, the polyurethane foam is soaked and then sintered to form a porous iron-base body with three-dimensional reticulated structure. Sequentially, organic acid (of ascorbic acid series) is used to treat the surface to form the metallic complex compound, which can adsorb and store stinks by the further special chemical-treatment (generally by alkali). The metal iron provides the metallic complex compound with electrons to maintain its activity so that the deodorizing effect can last a very long time. Compared with active carbon, it can deodorize more quickly, so can be used in families, great buildings and shops as air purifiers, and in automobiles as deodorizers.

3.8. Biological materials

Some porous materials like porous titanium, which are harmless to human body and possess good compatibility, have been used a great deal in medical and health area. For instance, porous-titanium hip-joints are used in orthopaedy; porous-titanium planted tooth roots are used for the renovation of teeth; porous W-Cr-Ni alloy composites are used in compound heart valvulae.

Besides the functional uses mentioned above, porous metals also have many structural uses which have been energetically related in Refs. [4–6, 11, 17, 46, 66, 92, 100, 117, 130–144]. In addition, some other new applications have been developed since 1990s. Here are some examples: to apply porous wolfram to hot evaporation of silver or gadolinium (by means of injecting powder into porous body) [145], to use foamed copper as the matrix of viscoelastic body and low-temperature welding material [146], to use porous copper or nickel to measure the melting point of lead or Sn-Pb alloy [147], to use porous bronze to serve as the exhaust plug in casting moulds, and so on. Some applications are still in the period of research and development.

Thomas *et al.* [148] introduced a method to produce porous metallic composite materials, which can be described as "metallization of porous matrix → oxidation in gaseous oxidative plasma zone → reduction in gaseous reductive plasma zone". The matrix can be ceramics or polymer, and the metal can be lead, palladium, nickel, silver, gold-palladium alloy, copper and so on. These composite materials can be used in the field of electrochemistry to produce the sensors of gas and the electrode of fuel cells. They can also be used for common purposes, such as the catalyst of chemical reactions, the catalytic active surface of high specific surface area and chromatographic-analysis separators.

4. End-statements

There are many kinds of methods for producing porous metals. To sum up, they are all developed in the direction of high porosity, uniform structure and excellent mechanical properties for an even wide range of applications.

Just in a few applications like heat insulation, porous materials are needed to have not only high porosity but also closed cells. In most applications, porous materials are developed in pursuit of not only high porosity, but also high through-hole ratio and high specific surface area, on the premise of sufficient mechanical strength. Consequently, the performance of products will reach the best status. This not only results in the large scale production for the porous metallic materials with three-dimensional reticulated structure, but also makes its application rapidly popularize to nearly cover or somewhat widen that of traditional porous materials. For instance, these high porosity metals can serve in various filters, liquid mixers, catalysts or their supporters, electrodes of fuel cells and batteries of nickel-cadmium, nickel-hydrogen and lithium, cathodes of electrochemical process for electrosynthesis and heavy-metal recovery, heat exchangers, sound-damping materials, electromagnetic shielding materials, composite metallic materials, some structural materials available in aerospace industry and so on [28–30, 36, 44, 136, 139, 149–154].

These porous materials with high porosity are primarily produced by metallic deposition (e.g. electrodeposition), and can also be produced by special powder metallurgy technology [7, 10] or permeating casting method [155]. It is in fact that various methods for producing porous metals can also be used to produce high-porosity materials.

Generally speaking, high porosity metal is an excellent engineering material with broad prospects, and the improvement of the preparation technology and the research of the property are very significant on this kind of material.

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References

1. H. BRAY, *Engineering Materials & Design* **16**(1) (1972) 19.
2. D. C. DILLEY, *Machinery and Production Engineering* **125** (1974) 24.
3. G. J. DAVIES and SHU ZHEN, *J. Mater. Sci.* **18** (1983) 1899.
4. A. G. EVANS *et al.*, *Progress in Materials Science* **43** (1999) 171.
5. L. J. GIBSON and M. F. ASHBY, "Cellular Solids," 2nd ed. (Cambridge University Press, Cambridge, 1997).
6. M. F. ASHBY *et al.*, "Cellular Metals, a Design Guide" (Engineering Department, Cambridge University, Cambridge, 1997).
7. K. SIZIKI and T. NAKAGAWA, *Engineering Materials* **30**(10) (1982) 104.
8. X. Q. YU *et al.*, *Journal of Functional Materials* **24**(5) (1993) 438.
9. H. P. TANG and Z. D. ZHANG, *Rare Metal Materials and Engineering* **26**(1) (1997) 1.
10. P. Y. HUANG, "Principles of Powder Metallurgy" (Metallurgical Industry Press, Beijing, 1997) p. 1.
11. T. J. LU *et al.*, *Acta Mater.* **46**(10) (1998) 3619.
12. E. MAINE and M. F. ASHBY, *Advanced Engineering Materials* **2**(4) (2000) 205.

13. W. P. MINNEAR and B. P. BEWLAY, US Patent 5213612 (1991).
14. T. XUE, *Materials for Mechanical Engineering* **16**(1) (1992) 4.
15. K. MARUMOTO and M. TOKIO, JP 106907 (1996).
16. MPR, *Met. Powder Rep.* **April** (1997) 39.
17. H. D. KUNZE *et al.*, *Powder Metallurgy International* **25**(4) (1993) 182.
18. J. BAUMEISTER, German Patent DE 4018360 (1990).
19. J. BAUMEISTER and H. SCHRADER, German Patent DE 4101630 (1991).
20. S. KATZ and J. L. GREENE, US Patent 3694325 (1972).
21. I. MATSUMOTO *et al.*, US Patent 4251603 (1981).
22. B. J. XIA *et al.*, *Chinese Journal of Power Sources* **2**(1994) 4.
23. W. WANG, *Battery Bimonthly* **25**(4) (1995) 181.
24. W. H. ZHU *et al.*, *Chinese Journal of Powder Sources* **20**(1) (1996) 5.
25. G. X. YU, *Battery Bimonthly* **26**(2) (1996) 86.
26. D. KOHLER *et al.*, *J. Electrochem. Soc.* **137**(6) (1990) 1750.
27. M. OSHITANI, JP 18304 (1992).
28. M. HONDA *et al.*, JP 2795A (1992).
29. H. SUGIKAWA, JP 274869 (1990).
30. *Idem.*, JP 130393 (1991).
31. J. BABJAK *et al.*, EP 0402738 A2 (1990).
32. L. Q. ZHANG and F. H. CHANG, *Journal of Functional Materials* **27**(1) (1996) 88.
33. E. KAMIJO *et al.*, US Patent 4326931 (1982).
34. H. SUGIKAWA, JP 290792 (1989).
35. *Idem.*, JP 274895 (1990).
36. J. R. BRANNAN *et al.*, US Patent 5098544 (1992).
37. H. SUGIKAWA, JP 138792 (1995).
38. G. X. YU, *Battery Bimonthly* **25**(3) (1995) 140.
39. T. NISHI and M. HONDA, JP 31446 (1993).
40. L. WO *et al.*, *Battery Bimonthly* **21**(6) (1991) 9.
41. I. WATANABE *et al.*, JP 248491 (1994).
42. W. S. YIN, *Journal of Functional Materials* **27**(2) (1996) 97.
43. Q. C. GU *et al.*, *ibid.* **27**(2) (1996) 135.
44. Y. MAEDA and T. KAWAKOE, JP 109597 (1995).
45. M. IWASAKI *et al.*, JP 89697 (1988).
46. H. G. HANUSA, US Patent 3549505 (1970).
47. H. SUGIKAWA, JP 290792 (1989).
48. M. SAIKA *et al.*, JP 116196 (1992).
49. M. NISHIMOTO *et al.*, JP 73988 (1990).
50. F. YOSHIAKIRA *et al.*, JP 84519 (1994).
51. T. R. THOMAS and J. P. S. BADYAL, UK Patent, GB 2287720A (1995).
52. P. S. LIU *et al.*, *Mater. Sci. & Technol.* **16**(5) (2000) 575.
53. H. SUGIKAWA *et al.*, JP 274895 (1990).
54. *Idem.*, JP 130394 (1991).
55. *Idem.*, JP 130395 (1991).
56. S. SATOO *et al.*, JP 39714 (1996).
57. A. SOSNIK, US Patent 2434775 (1948).
58. J. C. ELLIOTT, US Patent 2751289 (1956).
59. L. M. NIEBYLSKI *et al.*, US Patent 3743353 (1974).
60. S. O. FIEDLER *et al.*, US Patent 2974034 (1961).
61. W. S. FIEDLER, US Patent 3214265 (1965).
62. Y. ZHANG *et al.*, *Materials Science Progress* **7**(6) (1993) 473.
63. S. AKIYAMA *et al.*, U.S. Patent 4713277 (1987).
64. I. JIN *et al.*, US Patent 4973358 (1990).
65. O. PRAKASH *et al.*, *Mater. Sci. Engng.* **A 199** (1995) 195.
66. A. E. SIMONE and L. J. GIBSON, *Acta Mater.* **46**(9) (1998) 3109.
67. Z. A. MUNIR, *Ceramic Bulletin* **67**(2) (1988) 342.
68. H. C. YI *et al.*, *J. Mater. Sci.* **24** (1989) 3449.
69. J. SUBRAHMANYAN and M. VIJAYAKUMAR, *ibid.* **27**(1992) 6249.
70. I. PBOROVINSKAYA, *Pure & Appl. Chem.* **64**(7) (1992) 919.
71. J. Z. SONG *et al.*, *Material Science & Technology* **5**(1) (1997) 1.
72. K. Y. ZHAO *et al.*, *Powder Metallurgy Technology* **15**(1) (1997) 26.
73. H. B. WANG *et al.*, *Journal of Functional Materials* **28**(2) (1997) 115.
74. V. I. SHAPAVALOV, US Patent 5181549 (1993).
75. V. I. SHAPAVALOV and A. G. TIMCHENKO, *Physics Metals Metallogr* **76** (1993) 335.
76. A. E. SIMONE and L. J. GIBSON, *Acta Materialia* **44**(4) (1996) 1437.
77. А. Г. Косторнов Порошк, *Мет.* (4) (1983) 53.
78. K. SIERADZKI and R. C. NEWMAN, EP 0392738 (1990).
79. A. A. DUBIKOVSKAYA *et al.*, *Sov. Mater. Sci.* **26**(3) (1990) 372.
80. W. SCHAEFER, *Gov. Res. Announc. Index* (1991) 2.
81. M. OTSUKA *et al.*, in Proceedings of the RASELM'91 on Science and Engineering of Light Metals (Tokyo, Japan, Oct. 1991) p. 999.
82. TAKAHARA and FUKUURA, EP 0559904 A1 (1993).
83. M. FUJITA *et al.*, *Titan. Zirconium (Jpn.)* **42**(4) (1994) 1.
84. K. M. LIU *et al.*, *Powder Metallurgy Technology* **7**(1) (1989) 39.
85. Y. X. LI *et al.*, *Rare Metal Materials and Engineering* **20**(4) (1991) 56.
86. H. S. TANG, *Materials Science and Engineering* **10**(1) (1992) 43.
87. C. R. ZHEN, *Shanghai Nonferrous Metals* **16**(5) (1995) 272.
88. S. BAN *et al.*, *SAE Trans. J. Mater. Manuf.* **104**(1995) 700.
89. G. C. ZHANG, *Titanium Alloy Messages* **3**(1997) 3.
90. G. GIOUX *et al.*, *International Journal of Mechanical Sciences* **42** (2000) 1097.
91. J. BAUMEISTER *et al.*, *Materials & Design* **18**(4/6) (1997) 217.
92. S. K. MAITI *et al.*, *Acta Mater.* **32**(11) (1984) 1963.
93. K. PANNKOKE *et al.*, in Proceedings of the 29th International Symposium on Automotive Technology and Automation (Florence, Italy, 1996) Vol.1, p. 645.
94. L. LORENZI *et al.*, in Proceedings of the Applications for Aluminium in Vehicle Design (Detroit, Michigan, USA, 1997) p. 23.
95. T. MORIMOTO and F. NAKAGAWA, UK Patent GB 2190417A (1987).
96. T. J. LU *et al.*, *Journal of Applied Physics* **85**(11) (1999) 7528.
97. Y. C. LIU, *Rare Metal Materials and Engineering* **5** (1989) 36.
98. M. NAOE, *Sumitomo Light Metal Technical Reports* **35**(3/4) (1994) 105.
99. F. X. HUANG *et al.*, *Materials Review* **11**(3) (1997) 18.
100. M. F. ASHBY *et al.*, "Metal Foams and Honeycombs Database, Granta Design" (1997).
101. D. Y. TZOU and J. LI, *Journal of Composite Materials* **29**(5) (1995) 634.
102. A. E. SIMONE and L. J. GIBSON, *Acta Mater.* **46**(6) (1998) 2139.
103. Y. SUGIMURA *et al.*, *Acta Mater.* **45** (1997) 5345.
104. H. BART-SMITH *et al.*, *ibid.* **46**(10) (1998) 3583.
105. G. X. YU, *Battery Bimonthly* **26**(2) (1996) 86.
106. Z. H. JING and Z. Y. JIANG, *ibid.* **21**(1) (1991) 6.
107. J. CHAUSSARD *et al.*, *J. Appl. Electrochem.* **16** (1986) 803.
108. J. M. MARRACINO *et al.*, *Electrochim. Acta.* **32** (1987) 1303.
109. S. LANGLOIS and F. COEURET, *Journal of Applied Electrochemistry* **19** (1989) 43.
110. *Idem.*, *ibid.* **19** (1989) 51.
111. *Idem.*, *ibid.* **20** (1990) 740.
112. *Idem.*, *ibid.* **20** (1990) 749.
113. A. MONILLET *et al.*, *ibid.* **23** (1993) 1045.
114. P. COGNET *et al.*, *ibid.* **26** (1996) 631.
115. K. SABURO *et al.*, *Electrochemistry and Industrial Physical-Chemistry* **65**(1) (1997) 57.
116. U. ATSUSHI *et al.*, *ibid.* **66**(2) (1998) 194.
117. Elsevier Science Ltd., *Met. Powder Rep.* (MPR) (1997) 38.
118. P. S. LIU *et al.*, *Mater. Sci. Technol.* **16**(3) (2000) 341.
119. *Idem.*, *Science in China* **E42**(3) (1999) 294.
120. *Idem.*, *Mater. Sci. Engng.* **A 268**(1) (1999) 208.
121. A. D. TOMSETT, *Diss. Abstr. Int.* **48**(11) (1988) N. P.
122. A. V. BARBOV *et al.*, *Zh. Priki Khim.* **68**(5) (1995) 915.
123. V. N. ANTSIFEROV *et al.*, *ibid.* **70**(1) (1997) 105.
124. A. N. PESTRYAKOV *et al.*, *J. Adv. Mater.* **5** (1994) 471.
125. V. N. ANTSIFEROV and A. M. MAKAROV, *Zh. Priki. Khim.* **69**(5) (1996) 855.
126. V. A. AMETOV and A. N. PESTRYAKOV, *ibid.* **67**(2) (1994) 306.
127. J. G. IBANEZ *et al.*, in Proceedings of the Electrachemical Technology Applied to Environmental Problems PV 95-12 (Reno, Nevada, USA, 1995) p. 102.
128. J. B. ZENG *et al.*, *Powder Metallurgy Technology* **10**(4) (1992) 282.

129. Y. W. ZOU, *ibid.* **9**(4) (1991) 252.
130. W. THIELE, *Met. Mater.* **6** (1972) 349.
131. L. A. ARBUZOVA *et al.*, *Tsvetn. Met.* **2** (1997) 62.
132. A. E. SIMONE and L. J. GIBSON, *Materials Science and Engineering* **A229** (1997) 55.
133. G. N. KARAM and L. J. GIBSON, *Int. J. Solids Structure* **32a** (1995) 1259.
134. *Idem.*, *Ibid.* **32b** (1995) 1285.
135. J. B. CHOI and R. S. LAKES, *Cell. Polym.* **10**(3) (1991) 205.
136. K. SHIOZAWA *et al.*, *J. Soc. Mater. Sci.* **41**(461) (1992) 246.
137. Y. SUZUKI *et al.*, European Patent EP 0424109(1990).
138. D. MAHRUS *et al.*, UK patent, GB 2200583A (1988).
139. K. SHIOZAWA and T. MIZUGUCHI, *J. Soc. Mater. Sci.* **39**(445) (1990) 1360.
140. Y. SUGIMURA *et al.*, *Acta Materialia* **45**(12) (1997) 5245.
141. A. M. HARTE *et al.*, *Advanced Engineering Materials* **2**(4) (2000) 219.
142. O. B. OLURIN *et al.*, *Mater. Sci. Engng. A* **269**(1/2) (2000) 136.
143. O. B. OLURIN *et al.*, *J. Mater. Sci.* **35**(5) (2000) 1079.
144. A. G. EVANCS *et al.*, *Current Opinion in Solid State & Materials Science* **3**(3) (1998) 288.
145. T. SHIBATA *et al.*, *Vacuum* **33**(3) (1990) 304.
146. C. P. CHEN and R. S. LAKES, *J. Mater. Sci.* **28**(16) (1993) 4288.
147. K. B. KHOKONOV *et al.*, *Teplofiz. Vys. Temp.* **33**(2) (1995) 325.
148. T. R. THOMAS and J. P. S. BADYAL, UK Patent, GB 2287720A (1995).
149. K. SHIOZAWA and T. MIZUGUCHI, *J. Soc. Mater. Sci.* **39**(445) (1990) 1360.
150. K. SHIOZAWA *et al.*, *ibid.* **41**(461) (1992) 246.
151. H. TAKAJO *et al.*, JP 248492 (1994).
152. F. X. HUANG *et al.*, *Journal of Functional Materials* **27**(2) (1996) 147.
153. M. TABEI *et al.*, JP 81800 (1996).
154. H. TAKAJO *et al.*, JP 248492 (1994).
155. X. Q. YU and D. P. HE, *Journal of Functional Materials* **27**(2) (1996) 171.

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